

A STUDY ON THE EFFECT OF pH ON THE GROWTH RATE OF L HISTIDINIUM MALEATE (LHM)- AN ORGANIC NONLINEAR OPTICAL CRYSTAL

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ABSTRACT

The present work reports the growth of L Histidinium Maleate (**LHM**) at different pH values by slow evaporation method. The crown crystals were subjected various characterization studies. Crystals belong to triclinic system. Absorption spectrum shows optical transparency. Thermal stability by TG-DTA. Nonlinearity from second harmonic generation.

Keywords : X-Ray Diffraction, FTIR analysis, SHG.

I.INTRODUCTION

New organic nonlinear optical crystals are synthesized and subjected to characterization for applications in the area of high speed information processing, optical communications, data storage and signal processing [1-3] since the organic materials have high non linearity than inorganics [4-6].

Optical crystals from amino acids have non linearity due to its chiral carbon atom. Among all amino acids L-Histidine possess high optical nonlinearity. Many nonlinear optical crystals from L-Histidine such as L- Histidinium nitrate and L- Histidinium acetate was reported [7,8]. L Histidinium Maleate was grown at different pH by slow evaporation method. From the grown crystals high optical quality L Histidinium Maleate was subjected to different characterizations like Xray diffraction, FTIR, Thermal, CHN, Conductivity, and NLO studies.

II.EXPERIMENTAL

The pH of the solution influence the growth rate and the quality of the crystals. Normally amino acids are amphoteric in nature. It can act both as

acid or a base and therefore affected by pH. L- Histidine is an important amino acid used in the biosynthesis of proteins. It has a carboxylic acid group, an α -amino group and an imidazole side chain which identifies L- Histidine as a positively charged amino acid at physiological pH.

L-Histidine and maleic acid were taken in the equimolar ratio. The compound was dissolved in a mixed solvent of ethanol and water. The solution was stirred well to reach homogeneous concentration. The homogeneous solution at pH 2.0 was made to evaporate at room temperature and the quality of the crystal was improved by successive recrystallization. The pH of the solution was increased from 2.0 to 3.5 by adding ammonium hydroxide.

The optical quality of L Histidinium Maleate was affected by the pH of the solution.

The pH value and the super saturation of the solution affect crystal size. The size of the crystal was analysed by varying the pH from 2 to 3.0 for a fixed growth rate of 12 days is shown in Fig 1.

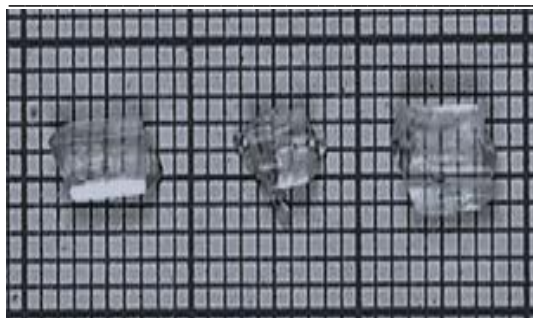


Fig.1 Single crystals of LHM

Though the optical quality of the crystals is affected by increasing the pH. The size of the crystals found to increase with increasing pH. A graph is plotted between the size and pH and is shown in Fig.2

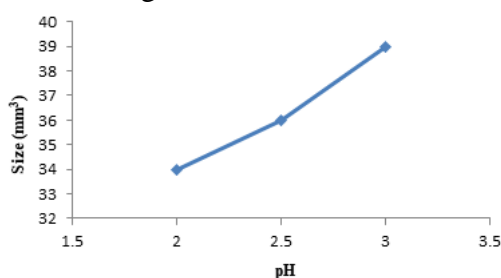


Fig. 2 Size of LHM as a function of pH

The graph clearly states that the size of LHM increases when the pH of the solution is increased from 2 to 3. The increase in size and the morphology of the crystal changes were due to the equilibrium concentration of different ions which drastically changes with the variation of pH and the supersaturation.

LHM crystal grown at pH 3.0 was optically good and employed for characterization studies.

III.RESULTS AND DISCUSSION

1. X-Ray Diffraction

Single crystal X-ray diffraction shows that L-Histidinium Maleate crystal belongs to the triclinic system. The cell parameters are $a = 7.22 \text{ \AA}$, $b = 9.89 \text{ \AA}$, $c = 12.94 \text{ \AA}$ and volume $V = 845 \text{ \AA}^3$.

Powder X-ray diffraction was carried out using a Reich-Seifert X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation and scanned over the range of 10° – 60° at a rate of $1^\circ/\text{min}$. The X-ray diffraction pattern of LHM is shown in Fig.3. Diffraction peaks were indexed for the lattice and the prominent peaks confirm the crystallinity.

2.Absorption Spectrum

The absorption spectrum of LHM was recorded using a Shimadzu UV-vis spectrophotometer and the spectrum is shown in Fig.4. It reveals that the lower cut-off wavelength is 285 nm. The crystal transparency was seen in the region from 400–800 nm which is an essential parameter for second harmonic generation[9].

3. FTIR Analysis

The presence of functional groups in the molecule was identified by FTIR and the spectral analysis was carried out using PerkinElmer Spectrophotometer in the mid IR region of 4000 cm^{-1} to 600 cm^{-1} by KBr pellet method is shown in Fig.5.

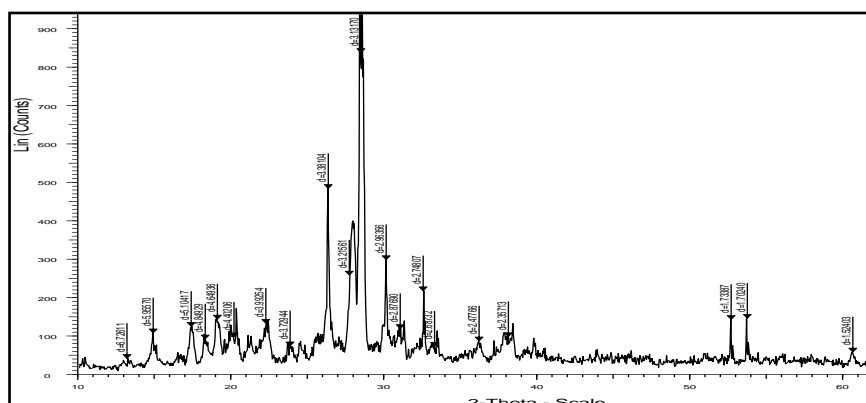


Fig. 3 X-ray Diffraction pattern of LHM

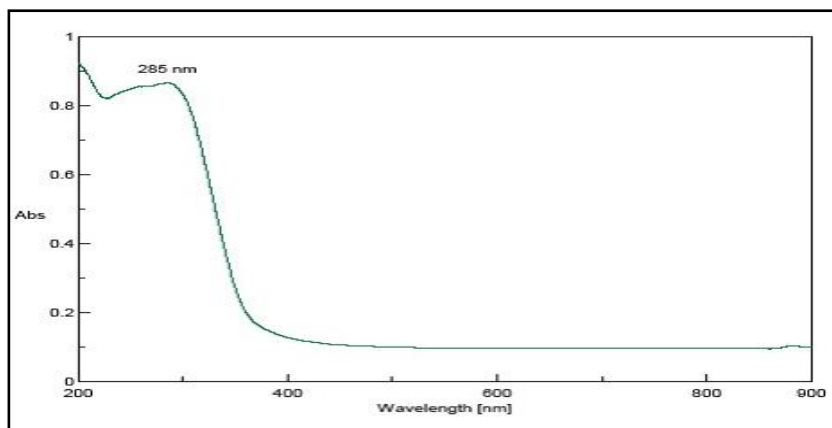


Fig. 4 Absorption Spectrum of LHM

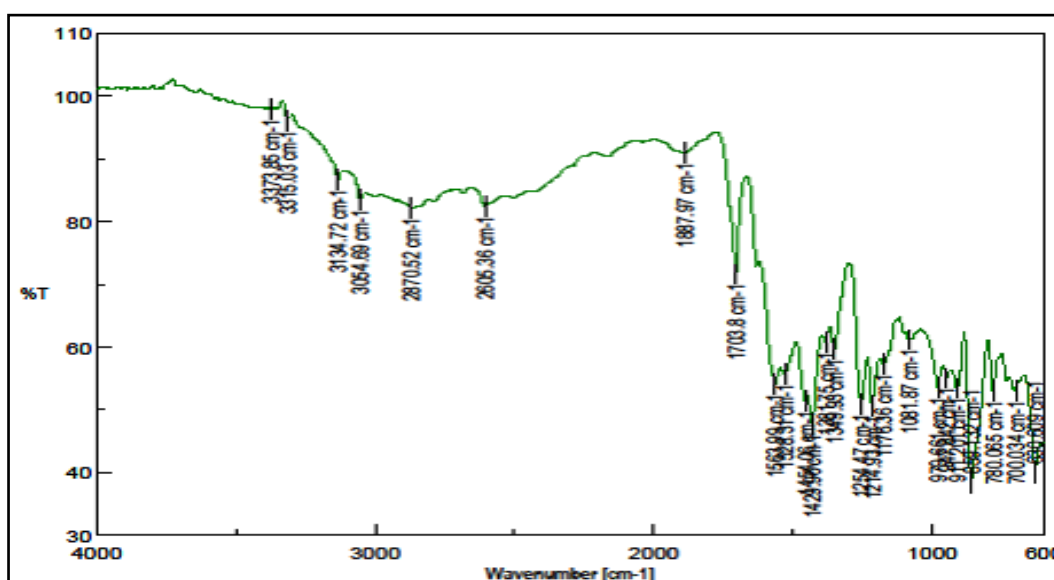


Fig. 5 FTIR Spectrum of LHM

The absorption peaks for different modes of vibration confirm the formation of LHM are indicated in Table 1.

Table 1. FTIR Frequency assignments of LHM

Band	Mode	Wave number (cm ⁻¹)
H-N-H	Symmetric stretching	3374
O-H	Symmetric stretching	3055
C-H	Symmetric stretching	2871
C=O	Asymmetric stretching	1704
C=O	Symmetric stretching	1564
H-O-H	Deformation	1454
C-N	Asymmetric stretching	1350
C-N	In plane bending	1082
C-O	Out of plane Deformation	780 and 630

4. Thermal Analysis

TG-DTA was analysed using ZETZSCH-Geratebau GmbH thermal analyzer. The powdered material was heated in a nitrogen atmosphere in an alumina crucible at the rate of 10°C/min. The TG- DTA thermogram of LHM is shown in Fig. 6.

TGA reveals that the material starts to decompose at 101°C and successive weight loss at 132°C, 185°C and 205°C. The volatility of the residual organic functional groups decide the weight losses. The melting point of the material was indicated by a sharp endothermic peak at 101.6°C. TG-DTA shows that the material is thermally stable up to 101.6°C.

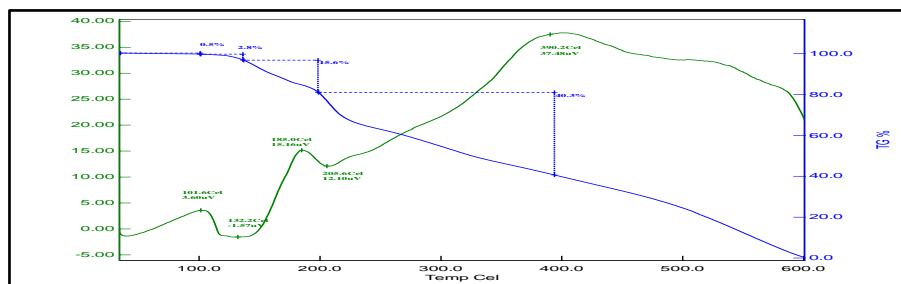


Fig.6 TG- DTA thermogram of LHM

5. Photoconductivity Measurement

Photoconductivity was studied by Keithley 485 pico ammeter. The photocurrent was measured by illuminating the sample with a halogen lamp which has iodine vapor. The photo current was recorded by increasing the voltage from 0 – 15.

A graph was plotted between photo current and applied voltage is shown in Fig. 7. The plot indicates that the photo current is increasing with the applied voltage. This shows LHM exhibit negative photo conductivity [10]. The reduction in the number of charge carriers of their life time is responsible for negative photo conduction.

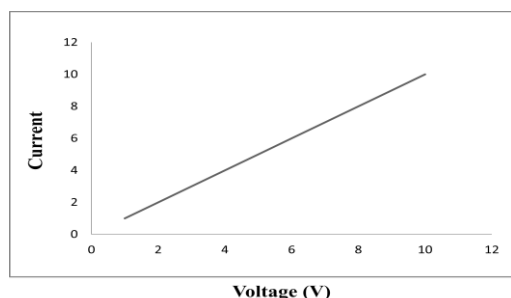


Fig. 7 Photoconductivity of LHM

6. CHN Test

The chemical composition of LHM was confirmed by CHN Test using Elementer Vario EL III CHNS analyser. The calculated values of carbon, hydrogen and nitrogen agreed well with

the experimental values which confirms the formation of LHM.

The results are given in Table 2

Table 2 CHN Analysis of LHM

Element Present	Composition (%)	
	Experimental	Calculated
Carbon	44.43	44.28
Hydrogen	4.93	4.83
Nitrogen	15.72	15.49

7. Photoluminescence Studies

The electronic structure of materials was studied by photoluminescence. The photoluminescence spectrum of LHM was recorded from 200 - 500 nm is shown in Fig. 8. The sharp intensity peak at 385nm implies near band-edge excitons of LHM which may be due to $n - \pi^*$ transition. Hence LHM finds applications in UV filters and optoelectronic laser devices.

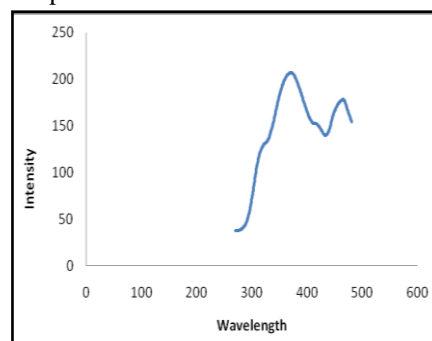


Fig.8 Photoluminescence spectrum of LHM

8.NLO Test

Non linearity was tested by Kurtz-powder method [11]. Nd:YAG laser beam of 1064nm was passed through the sample. The second harmonic signal generated in the powdered sample was confirmed by the emission of green radiation ($\lambda=532$ nm). Using KDP as a reference material it was observed that SHG efficiency of LHM was 1.5 times greater than that of KDP.

IV.CONCLUSION

L-Histidinium Maleate crystals were grown at different pH values by slow evaporation method. The crystallinity was confirmed by Powder X-ray diffraction. The crystal belongs to the triclinic system. Absorption spectrum indicates cut off wavelength is at 285nm. The crystal is thermally stable up to 101.6°C. LHM exhibit negative photo conductivity. CHN Test was analysed. The second harmonic efficiency was found to be 1.5 times greater than that of KDP.

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